



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (21) International Application Number: PCT/BR87/00004 (22) International Filing Date: 3 February 1987 (03.02.87) (31) Priority Application Number: PI 8600462 (32) Priority Date: 4 February 1986 (04.02.86) (33) Priority Country: BR (71) Applicant (for all designated States except US): MON-SANTO DO BRASIL S.A. [BR/BR]; Rua Paes Leme 524, 05424 - SÆo Paulo, SP (BR). (72) Inventors; and (75) Inventors/Applicants (for US only) : TEIXEIRA COSTA FILHO, Geraldo [BR/BR]; Rua Antonio Cesarino 474, Centro, 13100 - Campinas, SP (BR). VON ZUBEN, Fernando, José [BR/BR]; Rua Otimar Mergenther 15, apt. 25, Jardim Bela Vista, 13100 - Campinas, SP (BR). BERGSON FERNANDES BARRETO, Henri [BR/BR]; Rua Piquete 377, Nova Campinas, 13100 - Campinas, SP (BR). | | (74) Agent: DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA; Rua da Glória 366, 20241 Rio de Janeiro, RJ (BR). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), HU, IT (European patent), JP, LU (European patent), NL (European patent), NO, RO, SE (European patent), SU, US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: WATER SOLUBLE POWDER GLYPHOSATE FORMULATION (57) Abstract A novel water-soluble powder glyphosate formulation. | | |

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1.

Title: "WATER SOLUBLE POWDER GLYPHOSATE FORMULATION"

This invention relates to a novel watersoluble powdered glyphosate formulation.

Glyphosate (N-phosphonomethylglycine) is well-known in the art as an effective herbicide. It is known in the art that glyphosate, which is an organic acid, is relatively insoluble in water. Therefore, glyphosate is normally formulaed and applied as a water-soluble salt, especially as the isopropylamine salt. Various formulations of glyphosate are disclosed in U.S. Patents 4,405,531, 3,977,860 and 3,853,530. Roundup[®] Herbicide is the widely used commercial form of glyphosate and comprises the isopropylamine salt of glyphosate, surfactant(s), other adjuvants and water. Roundup[®] Herbicide is sold as a water-soluble concentrate.

It is desired in the art to find a water-soluble powder formulation of glyphosate which has the equivalent efficacy of Roundup[®].

Summary of the Invention

The present invention relates to a herbicidal water-soluble dry-particulate glyphosate formulation comprising the sodium salt of glyphosate and a surface active agent having the following formula:



2.

wherein R_1 and R_2 are independently methyl or ethyl;
 R_3 is methyl, ethyl, benzyl or C_{10} to C_{18} alkyl; R_4
 is C_{10} to C_{18} alkyl and X is chloro or bromo.

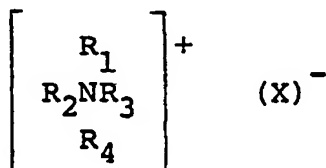
The water soluble powder formulation of the present
 5 invention has an efficacy substantially equivalent to Roundup®
 Herbicide. The powdered formulation will enable substantial
 savings in transportation and storage costs. A more thorough
 disclosure of the present invention is presented in the detail-
 ed description which follows.

10

Detailed Description of The Invention

The present invention relates to a herbicidal,
 water soluble dry-particulate glyphosate formulation compris-
 ing the sodium salt of glyphosate and a surface-active agent
 having the following formula:

15



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wherein R_1 and R_2 are independently methyl or ethyl;
 R_3 is methyl, ethyl, benzyl or C_{10} to C_{18} alkyl, R_4
 is C_{10} to C_{18} alkyl and C is chloro or bromo.

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The water-soluble dry-particulate glyphosate formu-
 lation of the present invention has herbicidal efficacy which
 is substantially equivalent to the commercial glyphosate
 formulation Roundup. Further, the formulation of the present
 invention is comparably efficacious at smaller surfactant to
 glyphosate rations than sodium glyphosate formulations com-
 prising the same surfactant(s) as used in Roundup Herbicide.
 This indicates that the surfactants of the present invention
 are more efficient in maintaining the sodium salt of glypho-
 sate in contact with the surface of the plant to facilitate
 penetration of the glyphosate into the plant than is the surf-
 actant(s) used in Roundup® Herbicide.

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Glyphosate is well-known to those skilled in the art. Several processes for the preparation of glyphosate are disclosed in the patent and chemical literature, e.g., U.S. Patents 3,977,860 and 4,486,358.

5 The powdered sodium salt of glyphosate (mono, di, sesqui) can be prepared by a variety of processes. First, the sodium salt of glyphosate can be prepared in accordance with the procedure set forth in U.S. Patent 4,140,513. Alternatively, glyphosate can be mixed with an alkali

10 base such as sodium hydroxide and the solution spray-dried to form the powdered sodium salt of glyphosate. Alternatively, the mono-sodium salt can be prepared by adding a solid alkali metal base with agitation to an aqueous slurry of N-phosphonomethylglycine containing

15 at least 50% solids.

Surfactants useful in the formulation of the present invention are commercially available from a number of manufacturers. Suitable surfactants are described in McCutcheon's Detergents and Emulsifiers,

20 North American Edition 1980 Annual and in McCutcheon's Detergent and Emulsifiers International Edition 1982. Suitable surfactants which are useful in the formulation of the present invention are alkyl-trimethyl ammonium chloride, alkyl-benzyl-dimethyl ammonium chloride and

25 dialkyl dimethyl ammonium chloride. The preferred alkyl-trimethyl ammonium chloride surfactant is cetyl-trimethyl ammonium chloride. Preferred cetyl-trimethyl ammonium chlorides are Emulgin IB-25, Drewfax 277, Dehyquat A and Dodigin 226. It will be obvious to one

30 skilled in the art that other surfactants within the scope of the present invention will also be useful. The formulations of the present invention are comprised of a dry, free-flowing particulate solid with varying particle sizes from powder to granules.

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Formulations of the present invention comprise the following ingredients:

| | <u>Ingredient</u> | <u>Wt %</u> |
|---|-------------------|-------------|
| 5 | sodium glyphosate | 5 to 95 |
| | Surfactant | 5 to 40 |

Preferred formulations are as follows:

| | <u>Ingredient</u> | <u>Wt %</u> |
|----|-------------------|-------------|
| | sodium glyphosate | 15 to 85 |
| 10 | surfactant | 5 to 20 |

The sodium salt of glyphosate useful in the formulation of the present invention will suitably have a water content of less than 3% by weight.

The formulations of the present invention may also be admixed with other additives such as urea, ammonium sulfate, silica, thickening agents, anti-foam agents such as silicones, water-repellants, humectants, chelating agents, dyes, dispersing agents, and other powdered active ingredients such as herbicides and fungicides or the like.

The formulations of the present invention can be readily diluted in water by the farmer in a spray tank prior to use. Suitable application rates of active ingredients will vary depending on plant species, but generally 90 to 360 grams per hectare on an acid equivalent basis will be suitable.

The following examples are presented to illustrate the present invention as well as some of the various embodiments of the invention. These examples are presented as being illustrative of the

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novel formulations and are not intended to be a limitation after the scope thereof.

Example 1

Typical formulation

| | | |
|----|---|-------------|
| 5 | | <u>Wt %</u> |
| | 1. monosodium glyphosate | 91.2 |
| | cetyl trimethyl ammonium chloride | 8.8 |
| | 2. monosodium glyphosate | 90.9 |
| 10 | alkyl dimethyl benzyl ammonium chloride | 9.1 |

Example 2

In this greenhouse test, two variety of difficult to kill plants prevalent in Brazil were treated with formulations of the present invention, Brachiaria (a narrow leaf plant) and Euphorbia (a broad leaf plant). The mono-sodium salt of glyphosate was tank-mixed in water with the indicated surfactant to provide indicated glyphosate concentration as set forth in the following tables. "A" designated trade secret surfactant(s) used in Roundup® Herbicide. "B" designates a surfactant chemically identical to "A" but produced by a different manufacture.

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Table I

| <u>Test 1</u> | | | | | | | |
|-------------------|---------------|-------------------|-------------|------------------------|---------------|----|------|
| | Rate | | Surfactant | <u>Percent Control</u> | | | |
| | Glyphosate** | | | Brachiaria | Euphorbia | | |
| | <u>(g/ha)</u> | <u>Surfactant</u> | <u>Rate</u> | <u>(DAT)</u> | <u>(DAT)*</u> | | |
| 5 | 360 | Drewfax 277 | 90 | 99 | (20) | 69 | (20) |
| | " | " | 180 | 99 | " | 74 | " |
| | " | Emulgin IB-25 | 90 | 95 | " | 63 | " |
| | " | " | 180 | 97 | " | 67 | " |
| 10 | " | B | 90 | 97 | " | 74 | " |
| | " | " | 180 | 100 | " | 80 | " |
| | " | Roundup® | | 99 | " | 80 | " |
| <u>Test 2</u> | | | | | | | |
| | 360 | Emulgin IB-25 | 90 | 96 | (21) | 41 | (21) |
| 15 | " | " | 180 | 97 | " | 66 | " |
| | " | Dehyquat A | 90 | 92 | " | 49 | " |
| | " | " | 180 | 100 | " | 67 | " |
| | " | A | 90 | 98 | " | 59 | " |
| | " | " | 180 | 96 | " | 62 | " |
| 20 | " | B | 90 | 98 | " | 64 | " |
| | " | " | 180 | 98 | " | 71 | " |
| | " | Roundup® | | 100 | " | 73 | " |

* Days after treatment

** Acid equivalent basis

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Table II

| Surfactant | | | Ratio Glyph*:Surf | Percent Control | | | |
|--------------------|-------------|-------------------|----------------------|-----------------|--------|--------|----|
| Commercial Name | Common Name | BRACHIARIA | | EUPHORBIA | | | |
| | | 10 DAT | | 21 DAT | 10 DAT | 21 DAT | |
| 5 | Emulgin | cetyl-trimethyl | | | | | |
| | IB-25 | ammonium chloride | 1:0.06 | 83 | 92 | 53 | 69 |
| | " | " | 1:0.13 | 86 | 97 | 58 | 74 |
| | " | " | 1:0.19 | 96 | 99 | 60 | 72 |
| 10 | Dodigen 226 | alkyl-benzyl- | | | | | |
| | | dimethyl ammonium | | | | | |
| | | chloride | 1:0.13 | 69 | 91 | 61 | 74 |
| | " | " | 1:0.25 | 78 | 96 | 59 | 75 |
| | " | " | 1:0.38 | 93 | 98 | 77 | 79 |
| 15 | Dodigen | dialkyl dimethyl | | | | | |
| | 1881 | ammonium chloride | 1:0.13 | 79 | 91 | 52 | 68 |
| | " | " | 1:0.25 | 87 | 97 | 63 | 71 |
| | " | " | 1:0.38 | 97 | 99 | 63 | 77 |
| | | Roundup® | | 97 | 99 | 50 | 75 |

* Acid equivalent basis

Table III
Application glyphosate concentration 360 g/ha (a.e.)

| | <u>Surfactant</u> | <u>Rate</u> g/ha | <u>Percent Control</u> | |
|----|-------------------|---------------------|------------------------|------------------|
| | | | <u>Brachiaria</u> | <u>Euphorbia</u> |
| | | | 21 DAT | 21 DAT |
| 5 | Emulgin IB-25 | 45 | 91 | 32 |
| | " | 90 | 93 | 47 |
| | " | 180 | 95 | 53 |
| 10 | A | 45 | 85 | 47 |
| | " | 90 | 95 | 56 |
| | " | 180 | 98 | 68 |
| | Roundup® | | 98 | 50 |

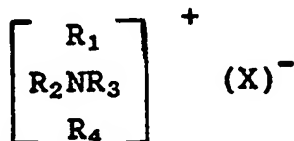
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Although this invention has been described with respect to specific embodiments, the details hereof are not to be construed as limitations, for it will be apparent that various equivalents, changes
5 and modifications may be resorted to without departing from the spirit and scope thereof and it is understood that such equivalent embodiments are intended to be included within the scope of this invention.

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WE CLAIM:

1. A herbicidal water-soluble, particulate formulation comprising the sodium salt of N-phosphonomethylglycine and a surface-active agent having the following formula:



wherein R_1 and R_2 are independently methyl or ethyl;
 R_3 is methyl, ethyl benzyl or C_{10} to C_{18} alkyl; R_4 is C_{10} to C_{18} alkyl and X is chloro or bromo.

2. The formulation of Claim 1 wherein the salt of N-phosphonomethylglycine is the monosodium salt.
3. The formulation of Claim 1 wherein the surface active agent is cetyl-trimethylammonium chloride.
4. The formulation of Claim 1 wherein the surface active agent is alkyl-benzyl-dimethylammonium chloride.
5. The formulation of Claim 1 wherein the surface active agent is dialkyl dimethylammonium chloride.

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6. A herbicidal, water soluble, particulate formulation comprising the monosodium salt of N-phosphonomethylglycine and a surface active agent having the following formula:



10 wherein R_1 and R_2 are independently methyl, ethyl; R_3 is methyl, ethyl, or benzyl or C_{10} to C_{18} alkyl; R_4 is C_{10} to C_{18} alkyl and X is chloro or bromo.

7. A herbicidal, water soluble, particulate formulation comprising the monosodium salt of N-phosphonomethylglycine and cetyl-trimethyl ammonium chloride.

INTERNATIONAL SEARCH REPORT

International Application No **PCT/BR 87/00004**

| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : A 01 N 57/20; A 01 N 25/30; A 01 N 25/14 | | | | | | | | | | | | | | | | | | | | | | | |
|--|---|-------------------------------------|---|--|---|---|---|-----|---|---|--|---|---|--|-----|--|--|---|--|--|---|---|--|
| II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: none;">Classification System </td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; vertical-align: top;">IPC⁴</td> <td style="border: none; vertical-align: top; text-align: center;">A 01 N</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div> | | | Classification System | Classification Symbols | IPC ⁴ | A 01 N | | | | | | | | | | | | | | | | | |
| Classification System | Classification Symbols | | | | | | | | | | | | | | | | | | | | | | |
| IPC ⁴ | A 01 N | | | | | | | | | | | | | | | | | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; font-size: x-small;">Category ⁹</th> <th style="width: 60%; font-size: x-small;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; font-size: x-small;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">EP, A, 0048436 (HOECHST) 31 March 1982, see page 4, lines 6-18 --</td> <td style="vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">EP, A, 0036106 (HOECHST) 23 September 1981, see claims 1-8 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">EP, A, 0039144 (ICI) 4 November 1981, see claims 1,3 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">P,X</td> <td style="vertical-align: top;">EP, A, 0206537 (STAUFFER) 30 December 1986 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 4528023 (J.L. AHLE) 9 July 1985 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">Chemical Patents Index, Basic Abstracts Journal, section C, 1986, Derwent Publications LTD. (GB), abstract no. 86-235747/36 & JP, A, 61165302 (NIPPON KAYAKU K.K.) 26 July 1986 -----</td> <td></td> </tr> </tbody> </table> | | | Category ⁹ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ | X | EP, A, 0048436 (HOECHST) 31 March 1982, see page 4, lines 6-18 -- | 1-5 | A | EP, A, 0036106 (HOECHST) 23 September 1981, see claims 1-8 -- | | A | EP, A, 0039144 (ICI) 4 November 1981, see claims 1,3 -- | | P,X | EP, A, 0206537 (STAUFFER) 30 December 1986 -- | | A | US, A, 4528023 (J.L. AHLE) 9 July 1985 -- | | A | Chemical Patents Index, Basic Abstracts Journal, section C, 1986, Derwent Publications LTD. (GB), abstract no. 86-235747/36 & JP, A, 61165302 (NIPPON KAYAKU K.K.) 26 July 1986 ----- | |
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| X | EP, A, 0048436 (HOECHST) 31 March 1982, see page 4, lines 6-18 -- | 1-5 | | | | | | | | | | | | | | | | | | | | | |
| A | EP, A, 0036106 (HOECHST) 23 September 1981, see claims 1-8 -- | | | | | | | | | | | | | | | | | | | | | | |
| A | EP, A, 0039144 (ICI) 4 November 1981, see claims 1,3 -- | | | | | | | | | | | | | | | | | | | | | | |
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| A | Chemical Patents Index, Basic Abstracts Journal, section C, 1986, Derwent Publications LTD. (GB), abstract no. 86-235747/36 & JP, A, 61165302 (NIPPON KAYAKU K.K.) 26 July 1986 ----- | | | | | | | | | | | | | | | | | | | | | | |
| <div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 48%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> | | | | | | | | | | | | | | | | | | | | | | | |
| IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">2nd June 1987</div> </td> <td style="width: 50%; border: none;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">- 8 JUL 1987</div> </td> </tr> <tr> <td style="border: none;"> International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none;"> Signature of Authorized Officer <div style="text-align: center;"> L. VAN MOL </div> </td> </tr> </table> | | | Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">2nd June 1987</div> | Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">- 8 JUL 1987</div> | International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center;"> L. VAN MOL </div> | | | | | | | | | | | | | | | | | |
| Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">2nd June 1987</div> | Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">- 8 JUL 1987</div> | | | | | | | | | | | | | | | | | | | | | | |
| International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center;"> L. VAN MOL </div> | | | | | | | | | | | | | | | | | | | | | | |

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/BR 87/00004 (SA 16170)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/06/87

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| EP-A- 0048436 | 31/03/82 | JP-A- 57082301 | 22/05/82 |
| | | DE-A- 3035554 | 06/05/82 |
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| | | AU-A- 5801486 | 04/12/86 |
| US-A- 4528023 | 09/07/85 | None | |